

Rapid At-Wavelength Inspection of EUV Mask Blanks by Photoresist Transfer

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Extreme-ultraviolet (EUV) lithography is an advanced form of optical projection lithography being developed by a consortium of integrated circuit manufacturers to print features $\sim 0.1 \mu\text{m}$ ^[1]. EUV lithography will likely employ a reflective mask consisting of a patterned absorber on a multilayer coated substrate (mask blank) that reflects a narrow band of EUV wavelengths near 13.4 nm. Such masks have the advantage of being thick and dimensionally stable, however, the use of such masks presents some challenges. Because it is currently impossible to repair certain types of defects in a mask blank, it will likely be necessary to begin with a defect free mask blanks. An effort is being made to produce defect free blanks^[2]. Blanks with as few as three defects, as determined by optical means, have been produced.

Unlike other existing and likely future technologies, optical inspection may not be sufficient to find all defects in an EUV mask. While optical inspection tools can be used to find certain defects (such as particles and scratches) on such a mask, subtle anomalies in the reflective

multilayer coating can produce dramatic changes in the real and imaginary components of the reflectivity at the EUV wavelength but have no apparent effect on visible light. Indeed, such defects have already been observed in EUV imaging experiments^[3]. Because of this, at-wavelength techniques, i. e. techniques using light of the wavelength at which the mask blanks are to be used, must be used to locate and mark defect sites. However, because optical inspection tools are so fast and efficient, it would be very economical to read out these marked defects optically. Therefore, we have developed a new EUV mask inspection technique in which defects are marked by a brief flood exposure to EUV radiation (from a synchrotron or laser-plasma point source) and then examined optically^[4].

In the simplest experimental arrangement for the new inspection technique, illustrated in **Figure A-1**, an EUV sensitive resist is deposited directly on the multilayer-coated mask blank. During a flood exposure, incoming EUV radiation passes through the thin layer of resist, reflects off the multilayer coating and then passes

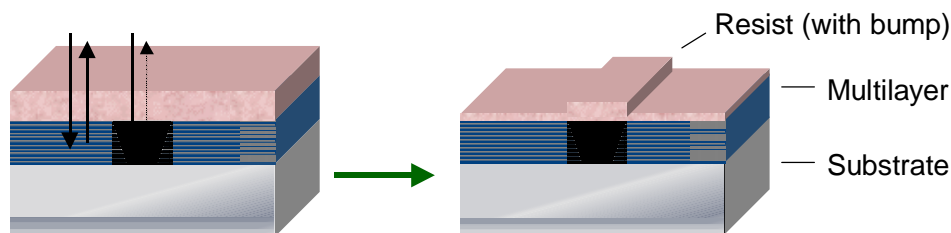


Figure A-1. Diagram illustrating the photoresist transfer process. a) A photoresist is applied directly to an EUV reflective multilayer coated substrate that is subsequently flood exposed with EUV radiation. A reflectivity defect results in less exposure to the resist above the defect. b) After partial development of a positive tone resist a bump remains above the defect.

back through the resist once again. A local decrease in reflectivity will reduce the resist exposure above defect sites. Under these conditions, partial development of the resist will show reflectance defects as mounds (pits) in a positive (negative) tone resist. Once the EUV flood exposure has created features in the resist immediately above defect sites, these mounds or pits can be detected by an optical scanning instrument, allowing rapid flagging of EUV defects.

The experiment was performed on an EUV mask blank, a 2" diameter Mo/Si multilayer-coated silicon wafer with a peak reflectance of 62% at a wavelength of 13.4 nm. To demonstrate the detection of known defects, reflectivity defects (of approximately 12% less reflectivity than normal) were created in the mask blank using a focused ion beam of Ga⁺. Before exposure, the multilayer-coated EUV mask blank was spin-coated with an 800 Angstrom thickness of ZEP resist and baked at 190°C for 1 hour. The exposure was performed with 13.4 nm radiation from the 3rd harmonic of the U13 undulator. Following EUV exposure, the sample was spin-developed in xylenes and rinsed in isopropyl alcohol.

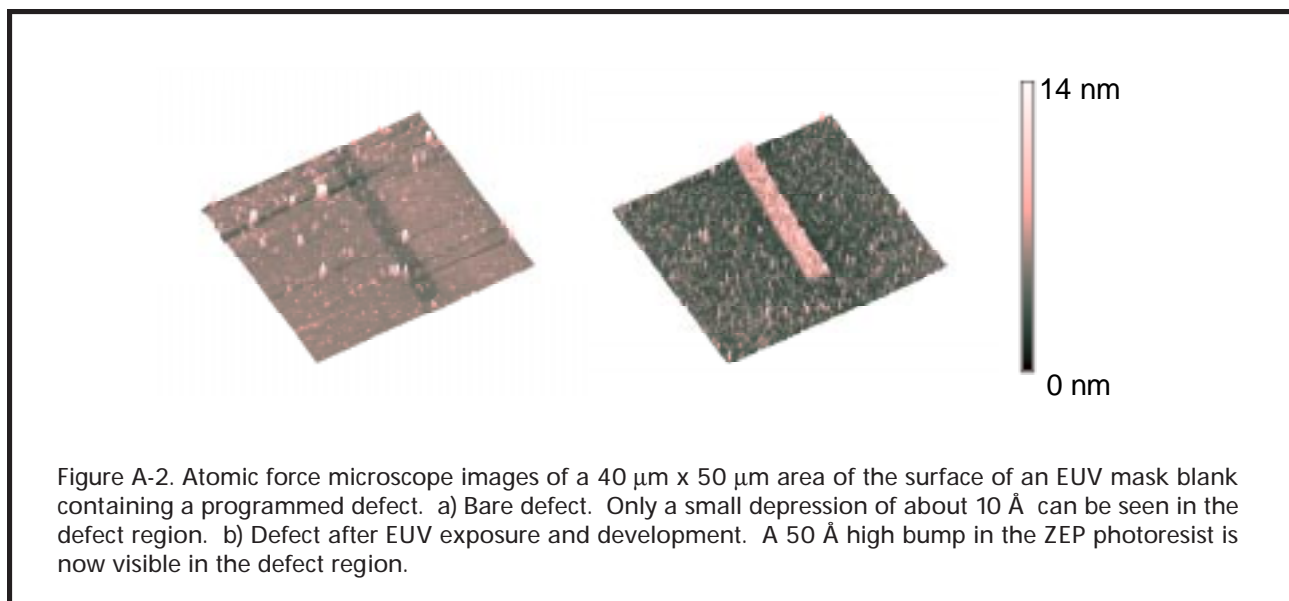
AFM images of an area of an EUV mask blank containing a programmed defect both before and after EUV exposure and development are shown in **Figures A-2a and A-2b**. In **Figure A-2a**, an AFM image of an area containing a bare programmed defect, there is a rectangular shaped depression in the surface of the multilayer coating in the implanted region approximately 10 Å deep. In **Figure A-2b**, an AFM image of the same area after EUV exposure and development, there is no longer a small depression; instead, there is a mound in the photoresist at the site of the defect approximately 40-50 Å high.

Current research efforts include the use of a higher contrast resist to create taller resist features. The taller features should be easier to detect, hence improving the sensitivity of our technique. Also currently being researched is an alternative technique which greatly reduces the risk of contaminating the mask blank. In this method, the resist is applied to a EUV-transmitting membrane which is placed in near contact with the mask blank during flood exposure. ■

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Atom-Specific Chemistry in Halogen Reactions with III-V Semiconductors

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Gaseous processes, such as plasma or reactive ion beam etching, are routinely used to fabricate structures for microelectronic devices. As device dimensions shrink and three-dimensional topography becomes more complex, however, these methods need to be better characterized and controlled. This requires that the gas-surface interactions be understood at the most fundamental level. Silicon etching is, by far, the system that has been the most widely studied, yet significant questions still remain. The situation for compound semiconductor materials is much worse^[1]. Despite their importance for photonic and electro-optic devices, factors affecting their processability by gaseous methods are poorly understood.

We have been using a number of surface-sensitive techniques, most notably synchrotron-based soft x-ray photoelectron spectroscopy (SXPS), to investigate the interaction of halogens with III-V semiconductor surfaces. Our group and others have found that not only are these reactions technically relevant, but there is also a rich chemistry involved. For example, ordered halogen overlayers form under certain conditions, while etching occurs under other conditions^[2]. Also, after large exposures at room temperature, surfaces are often covered with a thick halogenated reaction layer^[3].

Another useful by-product of our work has been the identification of methods whereby particular surface structures can be prepared in a simple manner via dry

chemical methods, i.e., without the need for a complex and expensive procedure such as molecular beam epitaxy (MBE). For example, we showed how to prepare high-quality GaAs(110) surfaces by reaction with Cl₂ at elevated temperature^[4], and how to prepare a group V-terminated (001) surface by saturating a group III-terminated surface with I₂ and then annealing^[2,5,6]. These methods of surface preparation can now be developed for use in other applications.

Most of our work has been with the (001) surface. This surface can be prepared to be either group III- or group V-terminated, so that the relationship between the surface termination and the reaction pathway can be directly determined. Note that this is also the surface employed for the fabrication of devices. We have used low energy electron diffraction (LEED) to measure the ordering and SXPS to determine the bonding configuration on the surface.

One of the remarkable observations is that, at room temperature, halogen adsorption on certain III-V semiconductor surfaces forms ordered overlayers, while other surfaces become disordered. The disorder is presumably the precursor to etching. Sometimes these complementary reaction pathways are obtained from initial surface conditions that are not too different from each other. **Figure A-3** summarizes whether particular (001) surfaces become ordered or disordered following a moderate exposure to I₂ or Cl₂, as determined by LEED.

Material	I ₂		Cl ₂	
	<u>Group III-Terminated</u>	<u>Group V-Terminated</u>	<u>Group III-Terminated</u>	<u>Group V-Terminated</u>
InAs	Order	Disorder	Disorder	Disorder
InSb	Disorder	Disorder	Disorder	Disorder
GaAs	Order	Order	Disorder/ Order	Disorder

Figure A-3. The experimentally determined reaction pathways of various III-V (001) surfaces when exposed to I₂ and Cl₂.

As can be seen, chlorine will almost always induce disorder (given sufficient exposure), while iodine sometimes orders and sometimes disorders.

There are a few factors that appear to control most of the observed behavior. For one, the various surfaces have different relative amounts of group III vs. group V atoms directly exposed to the incoming reactants. Note that, although a surface may be terminated with one element, there are most often vacancies in the first layer which expose some of the second layer atoms. Next, there is always a preference for reaction with group III, rather than group V, elements. On the reconstructed surface, group III elements have empty orbitals that protrude into the vacuum, while group V elements have filled lone pairs. The closed-shell halogen molecular orbitals are attracted to the empty surface orbitals, while they are repelled by the filled surface orbitals. Thus, the bonding of halogens is more likely to occur at group III surface sites than at group V sites. The degree of preference varies from system to system, however. Finally, an inability to form higher halides can passivate surfaces with respect to further reaction following the formation of a single monolayer of adsorbates.

For I_2 reacted with InAs(001), there is a big difference in the reaction pathway for the two terminations^[2]. On the In-terminated surface, a well-ordered (1×1) structure forms in which all of the iodine is attached to In, mostly in the form of the monoiodide, i.e., InI. The As-terminated surface becomes disordered, however, and iodine attaches to both In and As. SXPS spectra collected from I_2 -reacted InAs(001) are shown in **Figure A-4**.

These observations can be explained by assuming that iodine initially bonds to the group III In atoms, whether they are in the first or second layer^[2]. On the In-terminated surface, iodine attaches to the

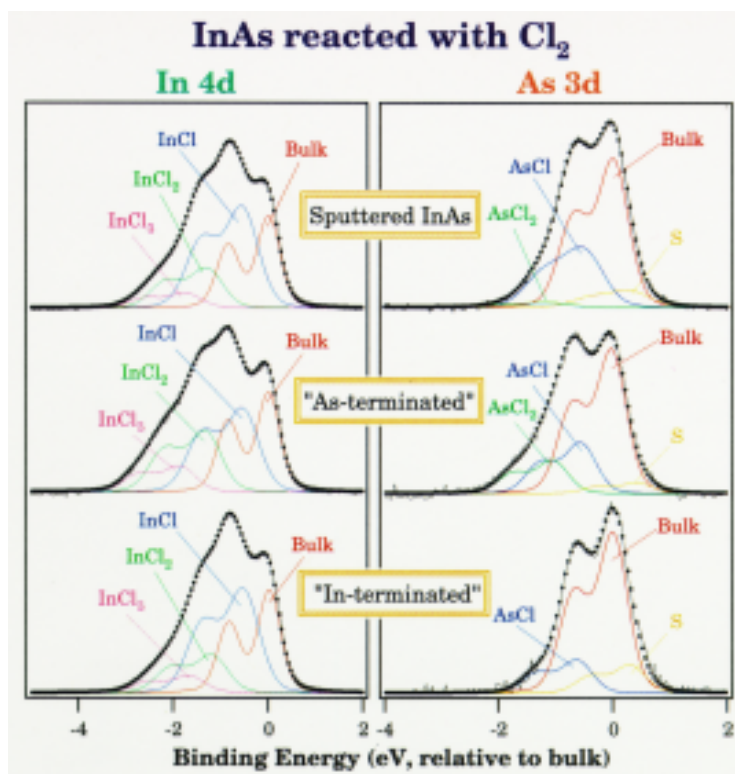


Figure A-4. High-resolution SXPS In 4d and As 3d spectra collected from In- and As-terminated InAs(001) after exposure to I_2 .

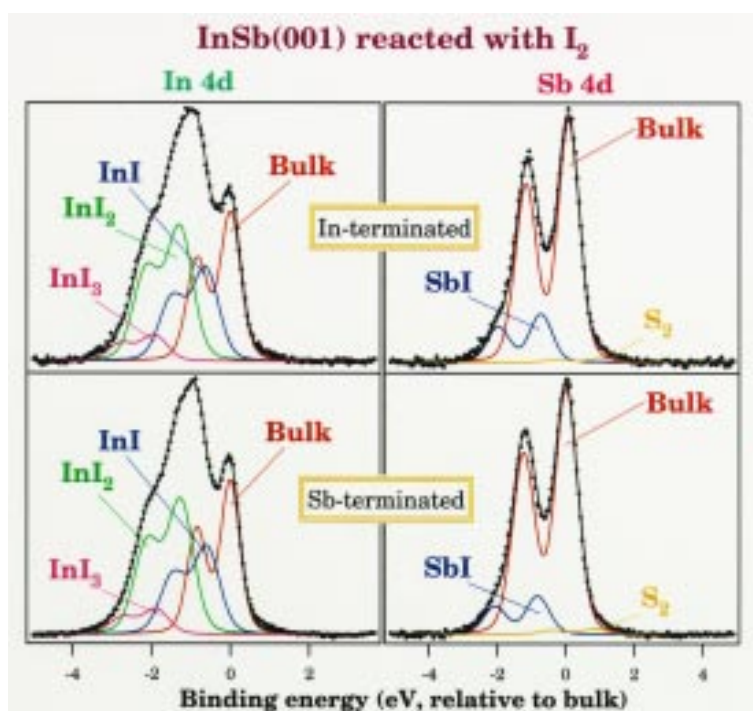


Figure A-5. Schematic illustration of the reaction mechanism for I_2 with In- and As-terminated InAs(001).

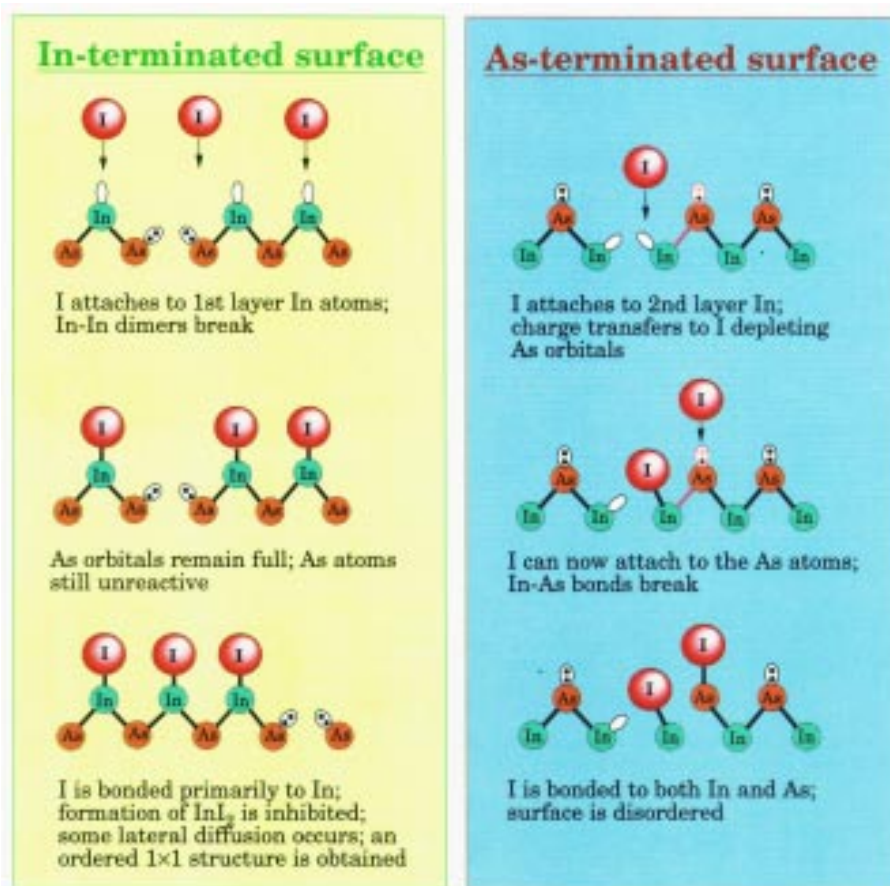


Figure A-7. High-resolution In 4d and As 3d core-level spectra collected after exposure of the indicated InAs(001) surface to Cl_2 .

outermost In atoms forming an ordered overlayer of monoiodides. This surface passivates, as the formation of diiodides is limited. On the As-terminated surface, on the other hand, iodine initially bonds to a second layer In atom. Upon bonding, charge is transferred away from the filled orbitals associated with surface As. This makes the first layer As atoms reactive to additional incoming I_2 . When iodine has bonded to both In and As, the In-As bonds break and the surface eventually becomes disordered. This mechanism is illustrated in **Figure A-5**.

On some surfaces, however, the preference for bonding to the group III element overwhelms all other factors. An example of this is given by the reaction of I_2 with InSb(001). As seen in **Figure A-6**, InI_2 is the major surface product, and the two terminations produce nearly identical spectra following reaction.

Cl_2 reactions appear to not be limited by either the preference for bonding to a group III atom, or by the stability of monohalides. Instead, it appears that chlorine can easily bond to either the group III or group V atom, and can easily form higher halides^[7]. This is seen in **Figure A-7**, which shows spectra collected from three InAs(001) surfaces following Cl_2 reaction. InCl is the primary species formed on all three surfaces, although some InCl_2 , InCl_3 , AsCl and AsCl_2 also form (AsCl_3 is volatile). On the initially As-terminated surface, relatively more of the higher In chlorides and As chlorides are produced. On the sputtered surface, however, relatively more In chlorides form, possibly because As was preferentially removed by the sputtering. Thus, although the relative amounts of the chlorides produced depend on the initial surface stoichiometry, the basic reaction pathway is essentially

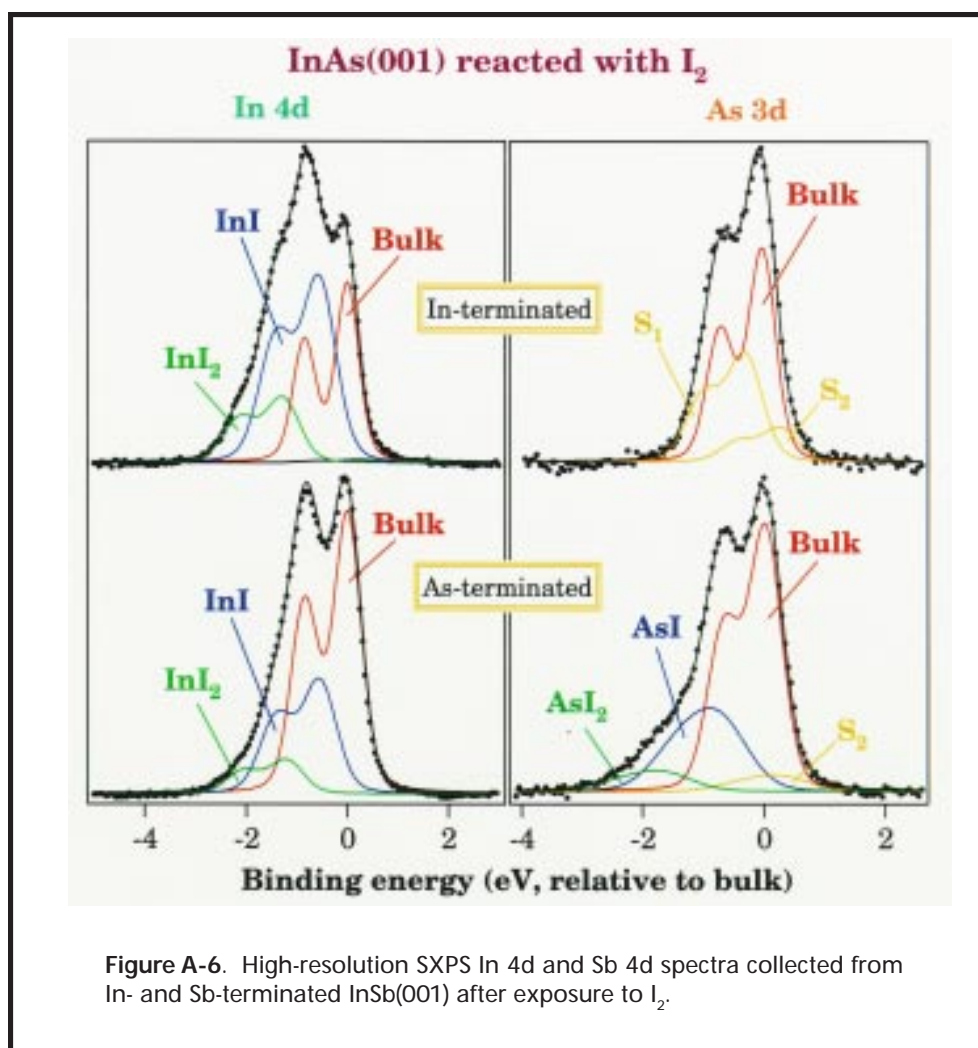


Figure A-6. High-resolution SXPS In 4d and Sb 4d spectra collected from In- and Sb-terminated InSb(001) after exposure to I_2 .

independent of termination. The same type of behavior is seen for Cl_2 reaction with GaAs(001) [8].

In summary, we have used synchrotron radiation and other surface-sensitive probes to enable a fundamental understanding of halogen reactions with III-V semiconductor surfaces. We found that the surface stoichiometry, and the relative ease of formation of the

higher halides determine the reaction pathway. These experiments (1) provide good basic physical and chemical insight into surface reactions, (2) will enable the development of a more rational approach to dry processing procedures, and (3) provide the understanding necessary for chemically producing surface structures with atomic precision. This last point will become even more crucial as the size scales on which we work get smaller. ■

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